Nitrosative Cleavage of 1-Acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine by Dinitrogen Tetraoxide

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The kinetics of formation of 1,3-dinitro-5-nitrosoperhydro-1,3,5-triazine show first-order dependence upon 1-acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine and upon dinitrogen tetraoxide. A mechanism involving attack by an ion pair is suggested. The product can be converted into 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) with nitric acid but this reaction is unlikely to involve an oxidation process.

NITROSATIVE cleavage has been studied by Bell and Dunstan [1] during their investigation of the chemistry of six-, seven-, and eight-membered cyclic nitramines. In all cases they found that mixtures of sodium nitrite and sulphuric acid were effective in converting *N*-acetoxymethyl derivatives into *N*-nitroso-derivatives [(Ib), (IIb), and (IIIb)]. We have previously [2] discussed the reactivity of the exocyclic *N*-methylene group with respect to nucleophilic substitution and have made only brief reference to the occasional concomitant electrophilic attack upon the attached nitrogen atom. We have used solutions of dinitrogen tetraoxide in carbon

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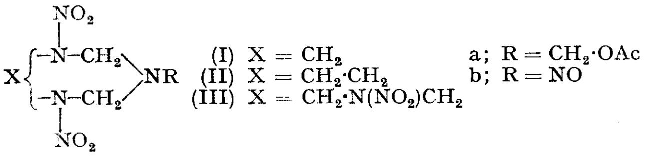
[1] J. A. Bell and I. Dunstan *J. Chem. Soc.* (*C*), (*a*) 1969, 1556; (*b*) 1969, 1559; (*c*) 1966, 862; (*d*) 1966, 867; (*e*) 1966, 870.

[2] T. G. Bonner, R. A. Hancock, and J. C. Roberts, *J.C.S. Perkin I*, 1972, 1902.

tetrachloride to introduce nitro-groups into aromatic systems and have shown[3] that this process involves electrophilic attack by the dinitrogen tetraoxide to



(I) $X = CH_2$ a; $R = CH_2{\cdot}OAc$
(II) $X = CH_2{\cdot}CH_2$ b; $R = NO$
(III) $X = CH_2{\cdot}N(NO_2)CH_2$

introduce a nitroso-group, followed by oxidation by nitrogen dioxide. It thus seems that we might bring about *N*-nitration and *N*-nitrosation by using the same reagent, and thereby define a route to the important cyclic nitramine, 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).

RESULTS AND DISCUSSION

In the absence of solvent, dinitrogen tetraoxide converted 1-acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine (Ia) in good yield into 1,3-dinitro-5-nitrosoperhydro-1,3,5-triazine (Ib). However in acetonitrile solution with only a 3-fold molar excess of dinitrogen tetraoxide the product was RDX (90%); only 3% of (Ib) could be isolated after reaction of a 0·03M-solution of (Ia) for 20 min. With dichloromethane, chloroform, or carbon tetrachloride as solvent and with various ratios of reactants only (Ib) could be isolated. In acetonitrile use of larger excesses of dinitrogen tetraoxide caused formation of more nitrosamine than RDX, *e.g.* a 5-fold excess gave 74% of RDX and 16% of (Ib) whereas a greater than 50-fold excess gave 90% of (Ib).

An n.m.r. study of solutions of 1-methoxymethyl- and 1-acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine in nitromethane upon the addition of dinitrogen tetraoxide indicated the formation of (Ib) together with methyl nitrate and nitronium acetate, respectively. The exocyclic *N*-methylene group was thought to give rise to formaldehyde but this could not be accounted for quantitatively, presumably because of loss from the solution and oxidation to formic acid (τ 2·0). Having obtained an indication of the stoicheiometry of the reaction, we carried out a kinetic analysis of the formation of the nitrosamine in order to clarify the mechanism and to explain the difference in behaviour of the reaction on changing to acetonitrile as solvent.

In order to follow the *N*-nitrosation in carbon tetrachloride solution directly by observing the appearance of the absorption at 370 nm ($\varepsilon = 66{\cdot}5$ l mol^{-1} cm^{-1}), concentrations of reagents were required for which the reaction was too rapid. Accordingly the technique of sampling was adopted and the product was estimated quantitatively after removal of the carbon tetrachloride by a colorimetric method based on a sensitive spot test.[4]

Preliminary results suggested a first-order dependence upon 1-acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine. With the same stoicheiometric concentrations of dinitrogen tetraoxide the *N*-nitrosation was faster at 20° than at 30°, suggesting that the reaction involved molecular dinitrogen tetraoxide and not nitrogen dioxide (Table 1). By making use of the molecular dissociation constant (K)[5] for dinitrogen tetraoxide in carbon tetrachloride at 30°, k_1 (the pseudo-first-order rate constant) was shown to depend upon $[N_2O_4]_{eq}$ (the equilibrium concentration) rather than upon the stoicheiometric concentration, $[N_2O_4]_{st}$ (Table 2). As the reaction was too rapid at concentrations greater than 15×10^{-5} mol l^{-1} it was not possible to test the first-order dependence over a wide range of concentrations of dinitrogen tetraoxide. With comparability in concentration of reactants the variation in dissociation of dinitrogen tetraoxide throughout the course of a kinetic run could not be neglected. Accordingly the second-order rate equation had to be defined thus:

TABLE 1

Temperature effect

$[N_2O_4]_{st} \times 10^5$/mol l^{-1}	k_1 (20°)/s^{-1}	k_1 (30°)/s^{-1}
7·75	4·58	4·01
9·15	6·08	4·92
10·40	7·41	5·57

TABLE 2

Dependence of rate constant on $[N_2O_4]$

$[N_2O_4]_{st} \times 10^5$/mol l^{-1}	$[N_2O_4]_{eq} \times 10^5$/mol l^{-1}	$k_1 \times 10^4$/s^{-1}	% Reaction followed	$k_1/[N_2O_4]_{st}$	$k_1/[N_2O_4]_{eq}$
6·50	2·46	2·93	12	4·51	11·9
9·10	3·96	4·98	19	5·47	12·6
10·25	4·67	6·92	23	6·75	14·8
13·65	6·89	10·00	35	7·32	14·5

k_1 = pseudo-first-order rate constant determined over limited % reaction. $[N_2O_4]_{st}$ = initial stoicheiometric concentration. $[N_2O_4]_{eq}$ = initial equilibrium concentration.

All experiments at 30° with [(Ia)] $1{\cdot}79 \times 10^{-5}$ mol l^{-1}.

$$dx/dt = k_2(a - x)[b - x + K/8 - \{K^2 + 16K(b - x)\}^{\frac{1}{2}}/8]$$

where a represents the initial concentration of (Ia) and b the initial value of $[N_2O_4]_{st}$. The integrated form * is then:

$$k_2t = \frac{16K}{N}\left[\ln(y^2 - 2Ky + K^2) - \ln\{y^2 - K^2 - 16K(b - a)\} - \frac{(2C + 2K)}{y - K} + \frac{D}{P}\ln\left|\frac{P + y}{P - y}\right|\right]^{Q}_{P'}$$

where $N = 128K(b - a)^2/\{K + 8(b - a)\}$ and
$P' = K^2 + 16K(b - x)$
$C = -K^2/\{K + 8(b - a)\}$
$P = K^2 + 16K(b - a)$
$Q = K^2 + 16Kb$
$D = \{K^2 + 16K(b - a)\}/\{K + 8(b - a)\}$

Values of k_2 were obtained by solving this equation for each value of x with the aid of a computer program.*

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* For derivation of the integrated form of the rate equation and the computer program for determining values of k_2 see J. C. Roberts, Ph.D. Thesis, University of London, 1971.

[3] T. G. Bonner and R. A. Hancock, *J. Chem. Soc.* (*B*), 1969, 1237.

[4] F. Feigl and C. Costa Neto, *Analyt. Chem.*, 1956, **28**, 1311.

[5] T. F. Redmond and B. B. Weyland, *J. Phys. Chem.*, 1968, **72**, 1626.

Results for a typical kinetic run are given in Table 3. The values of the second-order rate constants for different initial values of $[N_2O_4]_{st}$ both at 30° and at 20° are given in Table 4. The temperature dependence was small in comparison with the standard error in the rate constants; this precluded a meaningful determination of the activation enthalpy of the reaction. *C*-Nitrosation reactions have previously been examined[3] in carbon tetrachloride solution and although the reactions depend kinetically upon dinitrogen tetraoxide the latter behaves as a source of nitrosonium ions. To see if there was any similarity in the present case the nitrosations were carried out in the presence of antimony pentachloride. Considerable retardation of the reaction was observed with concentrations of the Lewis acid which were much lower than the initial value of $[N_2O_4]_{st}$, in contrast to the behaviour mentioned above. The interaction between antimony pentachloride and dinitrogen tetraoxide involves co-ordination with the nitrate ion, formed by heterolysis of the tetraoxide, causing an increase in the concentration of nitrosonium ion to a value above that from self-ionisation ($K_{20^\circ} = 4 \times 10^{-24}$ equiv.^{2} l^{-2}).[6] The mechanistic implication of the retardation is that the antimony chloride complexes (i) with the substrate, or (ii) with dinitrogen tetraoxide (if nitrosation occurs through the latter), or (iii) with nitrate ion, if the latter is involved in a rate-limiting ion-pair ($NO^+NO_3^-$) attack on the substrate. Since the dinitrogen tetraoxide and the substrate are in 200-fold and 30-fold excess, respectively, over the antimony pentachloride, the alternatives (i) and (ii) can be disregarded in favour of the ion-pair attack mechanism (Scheme 1). Some confirmation of this is provided by the low yields of (Ib) obtainable from (Ia) by using nitrosyl chloride in place of dinitrogen tetraoxide. Previously we have provided evidence for the lower nucleophilicity of chloride ion than nitrate ion in a non-polar medium.[2]

TABLE 3

Values of k_2 for a typical kinetic run

Time (t/s)	366	540	750	1032	1234	1512	1836	2076	2280	2604
10^5x/mol l^{-1}	0·485	0·768	0·997	1·162	1·308	1·462	1·525	1·585	1·620	1·701
k_2/l mol^{-1} s^{-1}	15·9	16·0	16·6	15·6	16·1	16·8	15·6	15·3	15·1	15·8

k_2(mean) = 15·9 (standard error 0·03).
a = 1·79 × 10^{-5} mol l^{-1}. b = 13·65 × 10^{-5} mol l^{-1}.

TABLE 4

Second-order rate constants at 20° and 30°

20°			30°		
Run	10^5b/mol l^{-1}	k_2/l mol^{-1} s^{-1}	Run	10^5b/mol l^{-1}	k_2/l mol^{-1} s^{-1}
19	4·88	11·1	1	3·96	15·6
27	5·45	15·3	12	5·20	15·2
18	5·58	13·8	11	6·50	16·6
16	6·10	12·4	10	7·79	14·3
25	6·86	14·2	9	9·10	13·9
14	7·13	11·3	7	10·25	17·7
24	7·55	14·7	6	11·52	14·0
23	8·27	15·0	5	12·80	16·7
22	9·69	15·7	4	13·65	14·2
21	10·38	16·3			

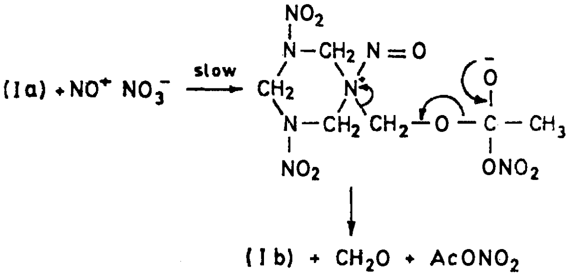
Mean value (20°) = 14·2 ± 2·1. Mean value (30°) = 15·0 ± 1·6.

TABLE 5

Effect of antimony pentachloride upon the rate constant at 20°

10^5b/mol l^{-1}	$10^7[SbCl_5]$/mol l^{-1}	k_2/l mol^{-1} s^{-1}
10·78		14·2
10·78	5·2	2·8

[(Ia)] = 1·79 × 10^{-5} mol l^{-1}.



SCHEME 1

When acetonitrile replaces carbon tetrachloride as solvent the interaction of acetonitrile with dinitrogen tetraoxide has to be considered:

$$n\,MeCN + N_2O_4 \rightleftharpoons [(MeCN)_n\,NO]^+\,NO_3^-$$

In dilute solution this equilibrium would be expected to favour the formation of the adduct and the concentration of free nitrosonium ion to be reduced so that reaction does not take place. However there is a concomitant increase in the concentration of nitrate ion, which may bring about nucleophilic substitution of the acetate group to form the nitrate ester. The elimination of formaldehyde and formation of RDX has been observed in the production of this nitrate ester from 1-chloromethyl-3,5-dinitroperhydro-1,3,5-triazine and silver nitrate.[2] With a large excess of dinitrogen tetraoxide in acetonitrile solution some formation of the nitrosamine would be expected together with RDX, as observed.

The inability of dinitrogen tetraoxide to oxidise (Ib) to RDX in any of the polychloromethane solvents or in acetonitrile contrasts with the behaviour of aromatic

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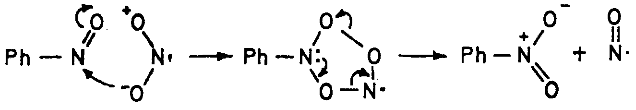
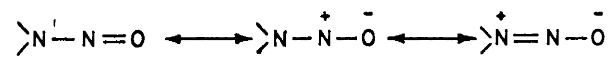
[6] R. S. Bradley, *Trans. Faraday Soc.*, 1956, **52**, 1255.

C-nitroso-compounds.[7] In the latter case nitrosobenzene was thought to be oxidised by nitrogen dioxide, with the latter behaving as a 1,3-dipolar reagent (Scheme 2). The difference in behaviour may be interpreted in terms of the reduction of the electrophilic nature of the nitrogen atom of the nitroso-group when this group is attached to another nitrogen atom rather than to a benzene ring:



SCHEME 2



Although a similar mesomerism may be envisaged to reduce the electrophilic character of the nitrogen atom of the nitroso-group in nitrosobenzene, this appears not to be so marked. Nitrosamines are well known to exhibit configurational isomerism as a consequence of the partial double-bond character of the N–N linkage, resulting in the non-equivalence of the alkyl groups of symmetrical dialkylnitrosamines as observed in their n.m.r. spectra.[8] All attempts by us to observe a similar behaviour with 1,3-dimethyl-2-nitrosobenzene failed to distinguish between the methyl groups even at temperatures as low as —50°.

Oxidations of some nitrosamines with a mixture of hydrogen peroxide and nitric acid[9] and with peroxytrifluoroacetic acid[10] have been reported. We have been unable to convert (Ib) into RDX quantitatively with peroxytrifluoroacetic acid, but have been successful using 100% nitric acid. Nevertheless here a nitration–denitrosation reaction is a possible alternative route to oxidation. A mass spectrometric examination of the RDX formed from (Ib) containing an ^{15}N-labelled nitroso-group and unlabelled 100% nitric acid revealed that the labelled nitrogen atom became detached from the ring nitrogen atom. In addition one of the nitro-groups becomes labelled when (Ib) is treated with ^{15}N-labelled nitric acid. The possibility of an exchange reaction cannot be entirely discounted but the results seem to indicate that the nitration–denitrosation is the favoured pathway.

EXPERIMENTAL

Materials.— 1-Acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine was prepared as described,[11] recrystallised from light petroleum (b.p. 40—60°)-acetone, and stored in a sealed tube at 0° prior to use. 1,3-Dinitro-5-nitrosoperhydro-1,3,5-triazine was prepared by the reaction of 1-methoxymethyl-3,5-dinitroperhydro-1,3,5-triazine with sodium nitrite and sulphuric acid.[1d] It was recrystallised from ethanol (twice) to give pale yellow needles, m.p. 158—165° (lit. values vary between 155° and 176°) (Found: C, 17·45; H, 2·85; N, 40·55. Calc. for $C_3H_6N_6O_5$: C, 17·5; H, 2·95; N, 40·75%). Sulphanilic acid (B.D.H. Laboratory Reagent) was recrystallised from hot water. α-Naphthylamine (B.D.H. Laboratory Reagent) was distilled at 86—90° and 1·0 mmHg to give a colourless liquid which solidified on cooling; m.p. 50° (lit.,[12a] 50°). Carbon tetrachloride was purified as described previously,[3] and acetonitrile was purified according to the method of Kevill.[13] Dinitrogen tetraoxide (Matheson Company) was mixed with a stream of oxygen and passed through a phosphorus pentoxide drying tower. It was collected and stored in ampoules until stock solutions in the appropriate solvents were required. Concentrations were accurately determined iodometrically without the use of an indicator. Nitrosyl chloride (Matheson Company) was used directly; it was stored in ampoules until required.

Reaction of 1-*Acetoxymethyl*-3,5-*dinitroperhydro*-1,3,5-*triazine with Dinitrogen Tetraoxide.*—(a) *In the absence of solvent.* The acetate (Ia) (0·5 g, 0·002 mol) was added to dinitrogen tetraoxide (3·5 g, 0·038 mol) at 0°. The solid dissolved and a green colour developed. After 5 min the oxides of nitrogen were removed by pumping into a cold trap (—180°), leaving a pale yellow solid. The yield of crude nitroso-product (Ib) after washing with dry ether was 0·35 g (85%).

(b) *In acetonitrile.* The acetate (Ia) (0·83 g, 0·003 mol) was added to acetonitrile (100 ml) containing 0·009, 0·015, or 0·15 mol of dinitrogen tetraoxide. The solutions were stirred at 0° for 20 min, after which the solvent and the excess of reagent were removed by rotary evaporation. The mixtures of (Ib) and RDX were separated by dissolving (Ib) in methanol (20 ml) and filtering off the relatively insoluble RDX (0·04 g in 20 ml). The yields were as follows: nitrosamine 3, 16, and 90%; RDX 90, 74, and 0%.

(c) *In carbon tetrachloride.* The acetate (Ia) ($1·8 \times 10^{-5}$M) and dinitrogen tetraoxide (4·0 and $18·0 \times 10^{-5}$M) were kept for 1 h at room temperature. After evaporation of the solvent the solid was analysed for (Ib) by the colorimetric method described later. 100% Conversion into the nitrosoamine was observed.

Reaction of 1-*Acetoxymethyl*-3,5-*dinitroperhydro*-1,3,5-*triazine with Nitrosyl Chloride.*—To a solution of the acetate (0·5 g, 0·002 mol) in dry acetonitrile (20 ml) was added a solution of nitrosyl chloride (excess) in acetonitrile at room temperature, slowly and with stirring. After 1 h volatile material was removed by rotary evaporation. Dry ether (8 ml) was added to the residue and the solid product filtered off. It was recrystallised from ethanol and identified as 1,3-dinitro-5-nitrosoperhydro-1,3,5-triazine (0·07 g, 17%).

Reaction of 1,3-*Dinitro*-5-*nitrosoperhydro*-1,3,5-*triazine with Nitric Acid.*—The nitroso-compound (Ib) (1·0 g, 0·0049 mol) was added very slowly and with continuous stirring to cold (—20°) 100% nitric acid (6·0 ml, 0·13 mol). The temperature was maintained at —10 to —20° throughout the addition and the solution turned deep yellow. The

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[7] T. G. Bonner and R. A. Hancock, *J. Chem. Soc.* (*B*), 1970, 519.

[8] G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, 1964, **86**, 4373.

[9] F. J. Brockman, D. C. Downing, and G. F. Wright, *Canad. J. Res.*, 1949, **27***B*, 469.

[10] W. D. Emmons, *J. Amer. Chem. Soc.*, 1954, **76**, 3468.

[11] W. J. Chute, A. F. McKay, R. H. Meen, G. S. Myers, and G. F. Wright, *Canad. J. Res.*, 1949, **27B**, 503.

[12] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, vol. IV, (*a*) p. 2390, (*b*) p. 2506.

[13] D. N. Kevill and R. F. Shutoff, *J. Chem. Soc.* (*B*), 1969, 366.

solution was then allowed to warm to room temperature and after 10 min was divided into two parts. Part 1 was cooled to −20° and poured slowly into cold (0°) water (15 ml). The precipitate was filtered off and washed with cold water (3 × 5 ml), cold methanol (2 × 5 ml) and finally ether (20 ml); yield 0·44 g (81·5%). The product was recrystallised from acetone and light petroleum and shown [i.r. spectrum, m.p. and mixed m.p. (201—203°)] to be RDX. Part 2 was evaporated at 1·0 mmHg leaving a white crystalline solid (0·51 g, 94·5%), similarly identified as RDX.

Kinetic Technique—Determination of 1,3-*dinitro*-5-*nitrosoperhydro*-1,3,5-*triazine*. Solution I consisting of 1% naphthylamine in aqueous 30% acetic acid was stored in the dark and used only up to a week after initial preparation. For preparation of solution II, concentrated hydrochloric acid was added slowly and with stirring to an equal volume of a 1% solution of sulphanilic acid in aqueous 30% acetic acid. This reagent was stored in the dark.

An appropriate volume of a solution of the nitrosamine (Ib) in carbon tetrachloride ($1{\cdot}343 \times 10^{-4}$M) was transferred to a flask [between 1·34 and $26{\cdot}9 \times 10^{-2}$ μmol of (Ib)]. The solvent was removed at 1 mmHg and the residue was treated with solution I (2 ml) followed by solution II (3 ml). The flask was then stoppered and kept at room temperature for 2 h. The intensity of a pink colour which had developed was measured at 530 nm in 10 mm glass cells, with a mixture of solutions I (2 ml) and II (3 ml) which had also been set aside for 2 h as reference. The development of the pink colour for 8×10^{-2} μmol of nitrosamine was shown to be complete in just under 2 h; no change was observed in the following 48 h. The presence of the acetate (Ia) proved not to interfere with the colorimetric estimation (ε_{530} $2{\cdot}41 \times 10^{4}$ l mol^{-1} cm^{-1}). The separate addition of solutions I and II from two burettes was found to give more reproducible results than mixing together prior to the addition of the nitrosamine.

Kinetic procedure. (Run 5) The acetate solution ($1{\cdot}12 \times 10^{-4}$M; 40 ml) which had been previously thermostatted at 30° was transferred to a flask fitted with a variable delivery automatic pipette (Jencons Co. Ltd.) modified to enable the plunger to be locked in the depressed position. Carbon tetrachloride (200 ml) at 30° was added and the reaction was started by the addition of the dinitrogen tetraoxide solution ($3{\cdot}2 \times 10^{-3}$M; 10 ml). At suitable intervals of time the reacting solution contained in the side tube of the automatic pipette was discarded and a fresh sample (6·12 ml) from the flask was drawn in and then expelled immediately into a vessel for removal of the solvent. The reaction time for each sample was taken as the time when evaporation of the carbon tetrachloride and oxides of nitrogen commenced. Using a rotary pump and a liquid nitrogen trap the maximum time required for the pumping at room temperature was 45 s. This represents only 1·3% of the total reaction time for the fastest kinetic run carried out. However owing to the preferential removal of the nitrogen dioxide, the time for stopping all reaction was probably less than 20 s.

The nitrosamine produced in each sample was determined by colorimetry as described above. The maximum optical density produced (0·526) corresponded to $1{\cdot}09 \times 10^{-7}$ moles of nitrosamine. This is equivalent to $1{\cdot}78 \times 10^{-6}$M (99·3%) in the reacting system.

N.m.r. Analysis.—Spectra were recorded with a Varian HA-60 Spectrometer. [$^{2}H_{3}$]Nitromethane was used as solvent and Me_4Si as internal standard. 1-Acetoxymethyl-3,5-dinitroperhydro-1,3,5-triazine [τ 3·9 (2H, s), 4·8 (4H, s), 5·0 (2H, s), and 8·1 (3H, s)] on addition of dinitrogen tetraoxide gave resonances at τ 1·5, 2·0, 3·7, 3·9, 4·3, and 8·0. 1-Methoxymethyl-3,5-dinitroperhydro-1,3,5-triazine [τ 3·9 (2H, s) 4·8 (4H, s), 5·8 (2H, s), and 6·9 (3H, s)] on addition of dinitrogen tetraoxide gave resonances at τ 2·0, 3·7, 3·9, 4·3, and 6·0. Three characteristic peaks are given by 1,3-dinitro-5-nitrosoperhydro-1,3,5-triazine owing to existence of *cis*- and *trans*-configurations of the *N*-nitroso-group with respect to the two methylene groups [τ 3·9 (2H, s), 3·7 (2H, s), and 4·3 (2H, s)]. The spectrum of a mixture of anhydrous nitric acid and acetic anhydride (nitronium acetate) in carbon tetrachloride showed the methyl protons at τ 7·93 and formic acid showed a resonance at τ 1·9.

1,3-*Dinitro*-5-[52% ^{15}N]*nitrosoperhydro*-1,3,5-*triazine*.—To a mixture of sulphuric acid (5 ml) and water (4 ml) at 5°, sodium [52% ^{15}N]nitrite (1 g) was added slowly. 1,1′-Methylenebis-3,5-dinitroperhydro-1,3,5-triazine (0·7 g), prepared according to the method of Dunstan [1d] and Wright,[11] was carefully added and the temperature was allowed to rise to 15°. After 15 min the mixture was poured into ice; the solid that separated was filtered off and recrystallised from methanol; yield 0·50 g, m.p. 166°.

Reaction with 100% *nitric acid*. To anhydrous nitric acid [14] (0·6 ml) at −10° the labelled nitrosamine (0·1 g) was added with stirring. The solution was poured into ice (4 g) and the solid filtered off and washed with water, methanol, and ether. The yield of RDX was 0·05 g.

100% [36% ^{15}N]*Nitric Acid*.—[36% ^{15}N]Nitric acid (41·3% w/w; 10 ml) was mixed with concentrated sulphuric acid (30 ml) and distilled at 1 mmHg in an apparatus fitted with a cold-finger (cooled with solid CO_2). The yield of 100% nitric acid was 3·6 g (72%).

The acid (0·6 ml) was treated with unlabelled (Ib) (0·1 g) as above.

[36% 1-$^{15}NO_2$]-1,3,5-*Trinitroperhydro*-1,3,5-*triazine*.—[36% ^{15}N]Nitric acid (100%; 2·3 g) was cooled to −30° and 1,1′-methylenebis-3,5-dinitroperhydro-1,3,5-triazine (0·2 g) was added with stirring. After allowing to warm to 30° the mixture was maintained at this temperature for 10 min, then cooled to −40°. Water (5 ml) was added, keeping the temperature below −10°. The labelled RDX was filtered off and washed with cold water, ethanol, and ether; yield 0·2 g.

Preparation and N.m.r. Spectra of 1,3-*Dimethyl*-2-*nitrosobenzene*.—1,3-Dimethyl-2-nitrosobenzene was prepared from 1,3-dimethyl-2-nitrobenzene (11·5 g) by a similar method to that used by us for 1,4-dimethyl-2-nitrobenzene [7] [yield 7·0 g, m.p. 140° (lit.,[12b] 141·5°)]. ^{13}C N.m.r. spectra were recorded on a Bruker HFX 90 spectrometer with Fourier transform facilities (solvent [$^{2}H_{2}$]dichloromethane; internal Me_4Si standard). The spectra showed no change between +30° and −50°: δ 18·8 (Me) and 129·2, 130·5, 132·9, and 142·2 (aromatic). The proton spectra were recorded on a Varian HA 100 spectrometer (solvent [$^{2}H_{2}$]dichloromethane; internal Me_4Si standard). Spectra showed no change between 30 and −50°: τ 2·9 (3H, m) and 7·6 (6H, s).

Mass Spectrometric Analysis.—Spectra and isotopic abundances were obtained with a Perkin-Elmer RMS 4 spectrometer; precise mass measurements were made with

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[14] T. G. Bonner and R. A. Hancock, *J. Chem. Soc.* (*B*), 1966, 972.

an A.E.I. MS 902 instrument by courtesy of the University of Kent at Canterbury. Measurements on compound (Ib) and its labelled derivative were made at *m/e* 132 and 133, respectively, corresponding to $C_2H_4N_3O_2(NO)$ containing the original nitroso-function. The peak height ratio $h_{133} : h_{132}$ was 49 : 42 (*i.e.* 54% labelled). Measurements on RDX were similarly made at *m/e* 205 and 206. $C_3H_5N_6O_5$ has a calculated mass of 205·0321363 and the observed mass was 205·0325405 (error 1·97 p.p.m.). The unlabelled sample had $h_{205}/h_{206} = 9·59$. The other samples of RDX gave peak heights as follows:

Origin of RDX	h_{205}	h_{206}	% ^{15}N in one nitro-group
Prepared from 1,1′-methylene-bis-3,5-dinitroperhydro-1,3,5-triazine	107	67	34·3
From labelled (Ib) with HNO_3	87·5	9·2	0·091
From (Ib) with $H^{15}NO_3$	74	50·5	36·64

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